30. FIRST TRANSITION SERIES ELEMENTS: FRACTIONAL CRYSTALLIZATION AND PARTIAL MELTING[1]

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INTRODUCTION

From a study of the first transition series elements we will try to define the pattern of fractional crystallization and partial melting. Results are discussed hole by hole in connection with lithological description and major element analysis, and element by element in term of fractional crystallization or partial melting using their partition coefficients.

THEORETICAL ASPECTS

Physicochemical Properties and Partition Coefficients

Crystal field theory shows that some transition metals are strongly stabilized in octahedric environments (Cr, Ni) while others are not stabilized (Ti, Zn) (Burns et al., 1970; Curtis, 1964; Orgel, 1964). From this theory, it is possible to infer that during partial melting or fractional crystallization highly stabilized elements will be concentrated in the solid phase, but it is impossible to deduce anything for others because nothing is known of the differences between their stabilization energies in solid and liquid phases. To examine the behavior of these elements, partition coefficients between minerals and glass were determined (Bougault and Hekinian, 1974, fig. 1) and found to be in good agreement with crystal field theory. Figure 1 presents partition coefficients for olivine, clinopyroxene, and plagioclase. Additional partition coefficients are being determined and will be published elsewhere.

From this theory in the first series of transition metals we expect to find the high partition coefficient (HPC) elements (Ni and Cr) and low partition coefficient (LPC) elements such as Ti and Cu. In fact, experimental values for tholeiitic basalts show little variation for Cu; the behavior of Cu cannot be fully explained only by these partition coefficients. As Ti is a minor element ($TiO_2 \cong 1\%$), before using this element as an LPC trace element it is necessary to verify that its behavior is similar to other LPC elements. It can be seen that the Ti partition coefficients found have the same order of magnitude as rare earths. Figure 2 shows a logarithmic plot of Dy normed to chondrites versus Ti for different samples including ophiolites (peridotite, gabbros, dolerite from Pindos, Vourinos, and Turquey) (Montigny et al., 1973), basalts from the FAMOUS area (personal communication from Treuil, IPG Paris), and one sample of Walvis Ridge (personal communica-

tion from Treuil, IPG Paris); Leg 37 samples are also plotted using values of Bryan et al., Dostal and Mueke, Schilling et al., Puchelt et al. (all this volume). All samples including basalts, dolerite, gabbro, and peridotite correlate except V8, A11, and K1 which are supposed to be residual phases (Montigny et al., 1973; Allègre et al., 1973) and the two peridotite samples of Site 334. This discrepancy can be explained by the fact that even small differences between Dy and Ti partition coefficients can produce significant differences in residual phase concentrations for a given step of partial melting. At this stage, it has only to be noticed that peridotite samples of Site 334 do not plot on the well-defined correlation line of gabbros and basalts; from some observations these peridotites are thought to be cumulates and the interpretation of their formation from a geochemical point of view must be considered taking into account their mineralogy and other chemical data.

Nevertheless, the fact that the slope of the straight line defined by log (Dy) versus log (Ti) for gabbros, some peridotites, and basalts is equal to one shows that Ti can be considered as an LPC element.

Partial Melting and Fractional Crystallization

There are at least two main ways to outline the extent of partial melting and fractional crystallization, using trace elements:

Hygromagnetophiles elements (Treuil, 1973). As crystallization proceeds, the ratio of the concentration in the liquid over the initial concentration in the liquid is given by the Rayleigh law:

$$\frac{C}{C_O} = F^{(D-1)}$$

where C = liquid concentration; C_o = initial liquid concentration; F = fraction of remaining liquid; and D = bulk partition coefficient.

For low partition coefficients, it can be approximated by:

$$\frac{C}{C_O} \cong \frac{1}{F}$$

The plot of the concentration of an element 1 versus the concentration of an element 2 is a straight line passing through the origin

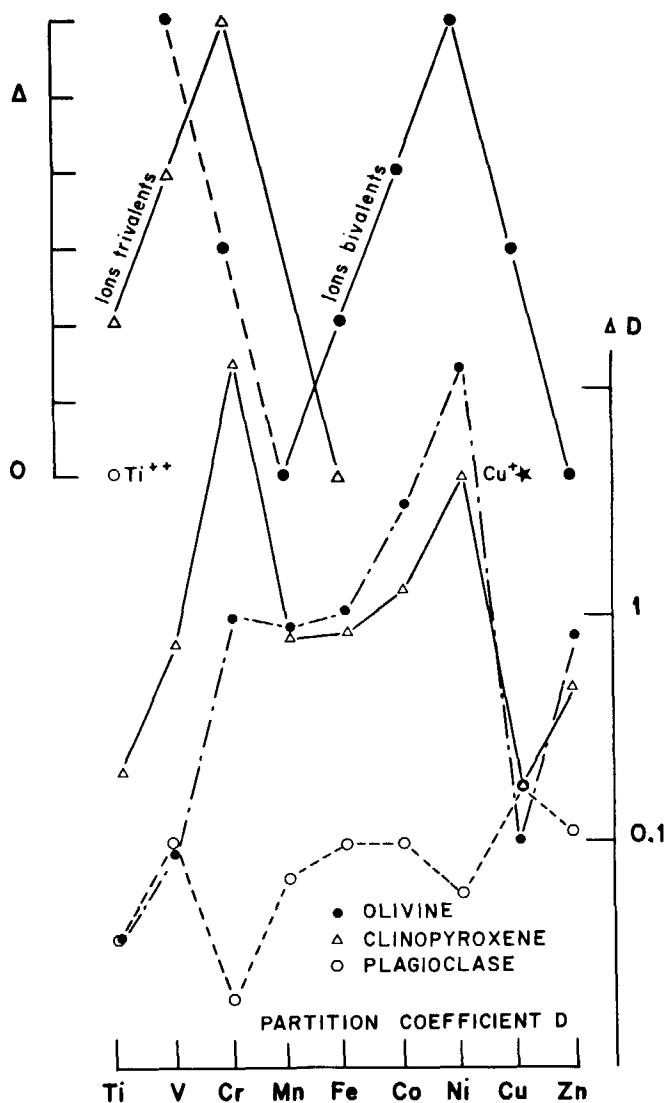$$C_1 = \frac{C_{01}}{C_{02}} C_2$$

Figure 1. *Stabilization energy.* △ *Partition coefficients versus atomic number.*

If different groups of samples are formed by the expression of fractional crystallization from different liquids produced by different steps of partial melting, they will plot on different straight lines, each group with a different slope C_{01}/C_{02}. This behavior has been shown clearly by Treuil. Each straight line characterized by its C_{01}/C_{02} is related to a given step of partial melting.

HPC and LPC elements. Using the Shaw formula (Shaw, 1970) giving the ratio of the concentration of an element in the liquid over the concentration in the initial solid as melting occurs,

$$\frac{Cl}{C_{OS}} = \frac{1}{D_O + F(1\text{-}P)}$$

where Cl = concentration in the liquid; C_{OS} = concentration in the solid; D_O = bulk partition coefficient of the initial assemblage; P = bulk partition coefficient with respect to melting phases; and F = fraction of liq-
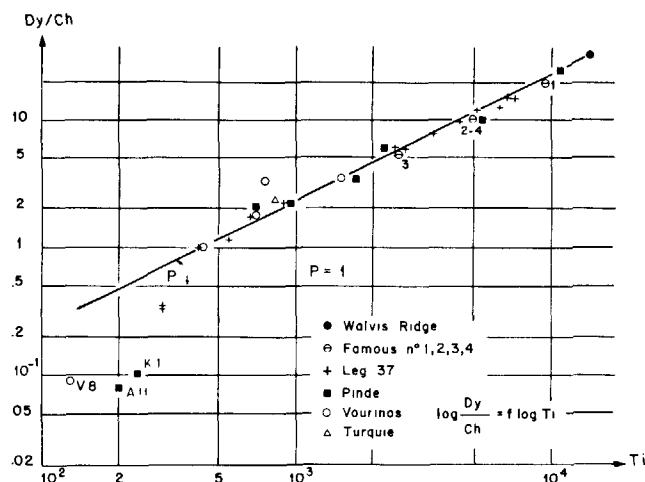

Figure 2. *Log Dy versus log Ti.*

uid produced. It can be shown that this ratio varies little for HPC elements: as an example, for melting an initial assemblage similar to the pyrolite of Ringwood (Allègre et al., 1973; Ringwood, 1966), this ratio would vary from 0.170 (F = 10%) to 0.280 (F = 20%) for Cr and from 0.109 (F = 10%) to 0.116 (F = 20%) for Ni. So we can assume Ni and Cr concentration to be constant in the liquid produced in a large range of melting.

Using the Rayleigh law $C/C_0 = F^{(D-1)}$ for Ni and Cr, it is possible to deduce F the remaining liquid fraction after crystallization, since C_0 the initial concentration in the liquid is assumed to be constant.

Knowing F, it is possible to calculate the initial concentration in the primary liquid of an LPC element (Ti).

$$Ti_O = \frac{Ti}{F^{(D-1)}}$$

where Ti_0 = initial concentration of Ti in the primary liquid. Thus, using a model of partial melting, it is possible to calculate the degree of melting from Ti_0 values.

As we have both HPC and LPC elements in the studied series, we will use this b method (Ni, Cr on one hand, Ti on the other). The method requires models for mineral assemblages, both for partial melting and fractional crystallization in order to calculate bulk partition coefficient from mineral partition coefficients. Discussion of the models and the details of the calculations will not be given in this report; only the results from Leg 37 samples are given assuming a simple hypothesis for mineral assemblages.

LEG 37 SAMPLES: DESCRIPTION OF RESULTS

The raw data for transition elements are presented in Chapters 2-5. Ti, Mn, and Fe analyzed as major or minor elements by XRF have been recalculated as ppm to have homogeneous results; the other elements were analyzed by atomic absorption and for Ni also by XRF. The first information given by these data is the confirmation of the different chemical units defined onboard by major elements analysis.

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Ti, Cr, and Ni values are plotted versus depth for Holes 332A (Figure 3), 332B (Figure 4), and 334 (Figure 5): a logarithmic scale is used for Cr and Ni because of the large variations of these elements from aphyric basalts to highly olivine phyric samples encountered.

Holes 332A and 332B

Chemical units defined onboard are confirmed, except in Hole 332A where chemical unit e has been divided into e1 and e2 on the basis of Cr and Ni data (Figure 3, Table 1): e1 and e2 correspond, respectively, to lithological Units 3b and 4. In 332A, plagioclase phyric units a and f are different on the basis of Ti as mentioned by Gunn and Roobal (this volume) as high Ti plagioclase phyric samples and low Ti plagioclase phyric samples and also on the basis of Cr and Ni; this

is clearer if we calculate trace element concentrations in the mesostasis (Table 2), plagioclase crystals having a dilution effect for transition elements (see partition coefficients, Figure 1). The last phyric unit g is well differentiated by Ni and especially by Cr ($\sim$750 ppm) due to clinopyroxene crystals in these samples (high partition coefficient).

Among aphyric units b, c, d, and e1 a remarkable point is the low concentration of Cr and Ni (b, c, d units). This point is discussed below.

In Hole 332B (Figure 4), same comments can be made for plagioclase phyric basalts of chemical unit a (low Ti) and unit d (high Ti); mesostasis concentrations of these samples are indicated also in Table 2, taking into account plagioclase dilution effect in respect of these elements in the bulk samples. Aphyric samples of Hole 332B, (b, c units) are similar to aphyric samples of
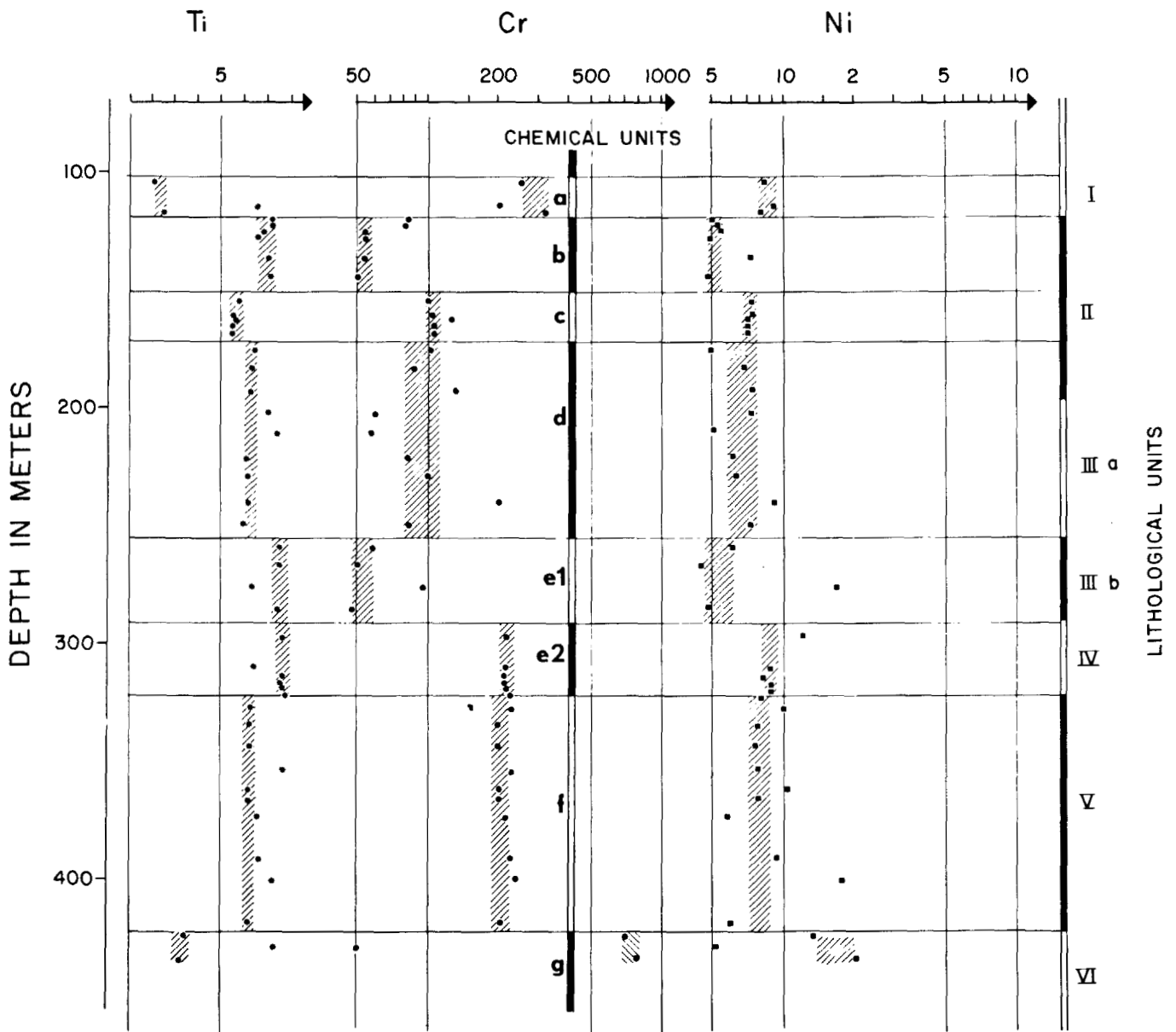

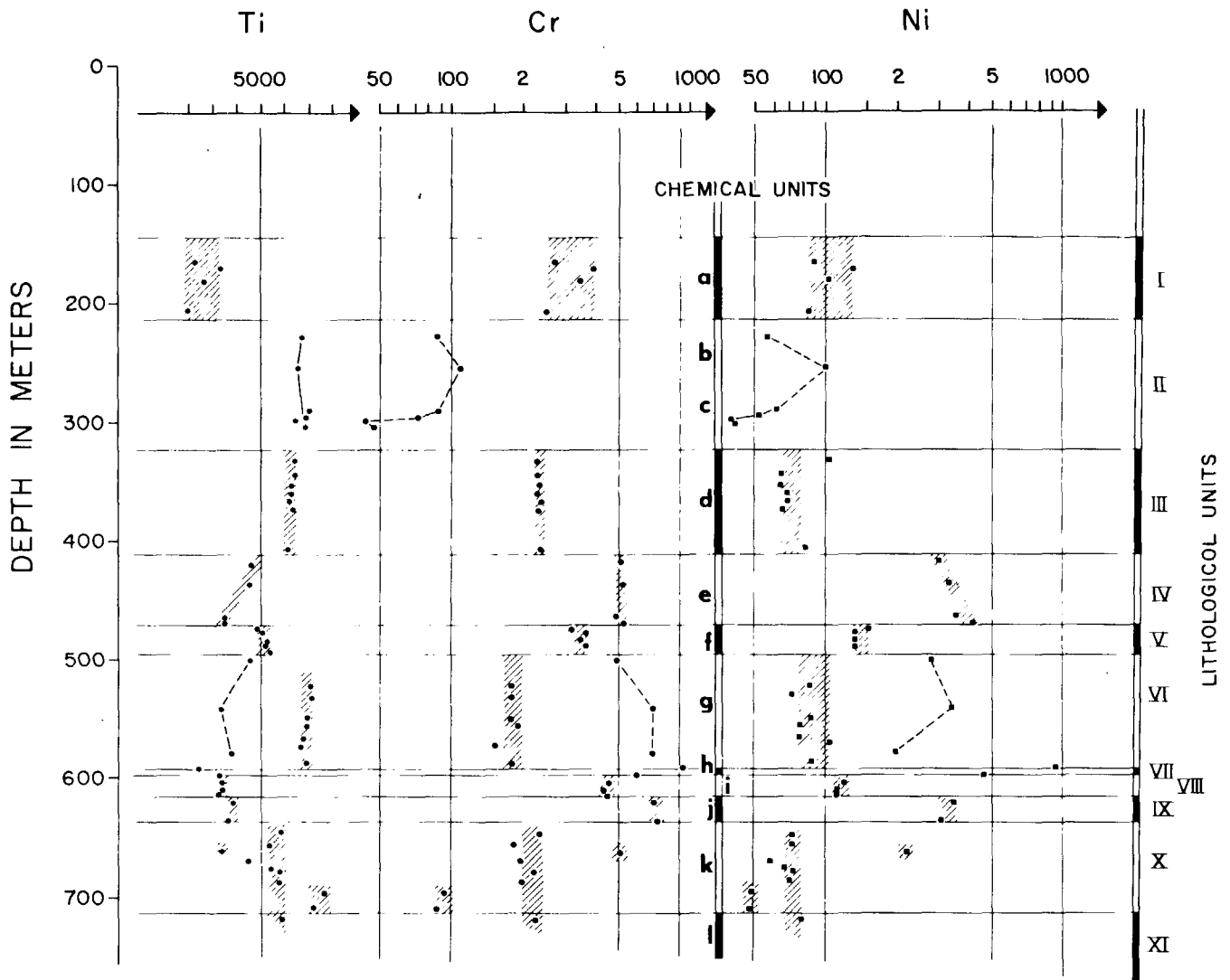Figure 3. *Hole 332A; Ti, Cr, and Ni versus depth.*

Figure 4. *Hole 332B; Ti, Cr, and Ni versus depth.*

332A. From these results, and down to unit d of 332B, the comparison between 332A and 332B indicated by Bougault (this volume) from major elements determined onboard is confirmed; there is a very strong chemical similarity between the following units:

332A	332B
a	a
bcd	bc
f	d

In Hole 332B, from unit e, as depth increases, we find different olivine phyric units very well differentiated by Cr and especially Ni because of the high partition coefficient of Ni in olivine (Figure 1). These units occur as units defined onboard (e, h, j), but also sporadically inside others units (Figure 4). Unit k is composed mainly of plagioclase phyric basalts probably similar to unit d, olivine phyric basalts (low Ti, high Cr and Ni) and aphyric samples similar to b-c units.

Hole 333A, mainly composed of aphyric basalts, shows variable concentrations of transition elements as depth increases: Ti varies from 3400 to 7800 ppm and Ni from 60 to 130 ppm. These results, together with major element data, indicate a lack of chemical continuity perhaps due to the abundance of basalt breccia and rubble in the section.

Figure 5 gives the variation of Ti, Cr, and Ni with depth in 334 and clearly shows the two upper basaltic layers a and b, and then in the mafic to ultramafic layer c gabbros, olivine gabbros, and peridotite are differentiated by their Cr, Ni content increasing from gabbros to olivine gabbros and peridotites reflecting the content of pyroxene (and chromite in peridotites) and olivine.

At Site 335 transition element concentrations are constant and confirm major element data indicating no chemical variation in this hole.

FRACTIONAL CRYSTALLIZATION AND PARTIAL MELTING

A first result is the qualitative agreement between stabilization by ligand field, partition coefficients and Leg 37 results shown by the chrondrite normalized diagram (Allègre et al., 1968; Figure 6) for chemical
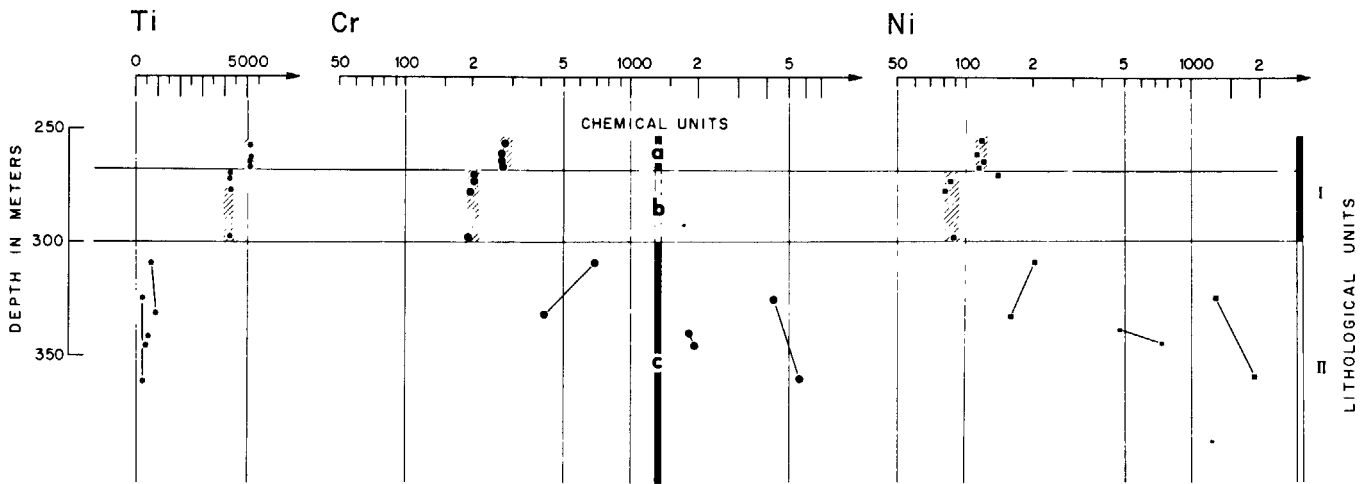
Figure 5. *Site 334; Ti, Cr and Ni versus depth.*

units b, c, d, e1 of Hole 332A: as crystallization proceeds, Cr and Ni are depleted and Ti and V increase significantly.

V following Ti, is a general feature in all samples studied and confirms that, in this kind of rocks, V can be considered as an LPC element as suggested by the partition coefficients found (Figure 1).

For Co, using the partition coefficients found and the model mentioned by Allègre et al. (1973), it can be deduced that Co concentration in the liquid is nearly constant for a large range of melting; the bulk partition coefficient for crystallization is nearly one; these two observations explain the Co values which were found to be in the narrow range of 40-50 ppm, except for olivine-phyric samples.

In order to explain quantitatively the behavior of Cr and Ni, it is necessary to choose samples representative of the liquid phase with little pyroxene and olivine: variable quantities of these crystals enriched in Cr and Ni comparatively to the groundmass would lead to inconsistent deductions. Only aphyric samples will be considered or plagioclase phyric samples taking into account the concentration calculated as plagioclase-free samples (no Ni or Cr in plagioclase). Glass from Sample 18, CC of Hole 332A and glasses of the FAMOUS area have the same composition as the associated rock matrix, both for major elements and transition elements.

Fractional Crystallization

First, we propose to show that Cr and Ni values are in agreement with the partition coefficients found: then we will try to evaluate the percentages of crystallization from a primary liquid.

The relation between the two elements as crystallization proceeds in the liquid phase is:

$$\log (Cr) = \frac{P_{Cr}-1}{P_{Ni}-1} \log (Ni)$$

$$+ \frac{(P_{Ni}-1) \log (Cr)_0 - (P_{Cr}-1) \log (Ni)_0}{P_{Ni}-1}$$

where (log Cr) = concentration of element in the liquid; (log Cr) = concentration of element in the initial liquid; P_{Cr} = bulk partition coefficient for Cr; and P_{Ni} = bulk partition coefficient for Ni.

The model chosen to calculate the partition coefficient is: crystallization of 60% plagioclase, 25% augite, 10% orthopyroxene, and 5% olivine (Allègre et al., 1973).

This gives P_{Cr} = 4.04, and P_{Ni} = 2.37.

Log (Cr) has been plotted versus log (Ni) in Figure 7; each point is the mean value for a chemical unit, corrected if necessary for plagioclase content. Olivine phyric samples have not been taken into account and would plot on the right of the diagram because of the high partition coefficient of Ni. One can note that the dispersion is small around the straight line representing log (Cr) = f (log [Ni]), and aphyric samples and plagioclase phyric samples (corrected for their content of plagioclase) remaining on the left side of the straight line are not very much differentiated in this diagram as previously thought from a few previous measurements (Bougault and Hekinian, 1974). The slope of this line, about 2.35, is in good agreement with the chosen model, which gives:

$$P = \frac{P_{Cr} - 1}{P_{Ni} - 1} = \frac{3.04}{1.37} = 2.22$$

This small difference and the small scatter of points around the line is probably a result of the small variation in mean crystallization of olivine.

This result is a verification of the ratio $P_{Cr} - 1/P_{Ni} - 1$; if we have samples coming from the same initial liquid and differing only by fractional crystallization, it is possible to verify the absolute values of P_{Cr} and P_{Ni}; for two samples 1 and 2, and from the Rayleigh law, it is possible to write

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TABLE 1
Mean Values of Chemical Units

	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Hole 332A									
a	2,340	150	292	700	37,525	29	83	72	29
b	6,920	293	55	1,300	78,000	43	55	77	74
c	5,640	265	110	1,180	67,950	43	73	89	63
d	6,480	272	82	1,225	71,820	42	65	80	68
e1	7,390	290	53	1,320	79,800	42	51	73	74
e2	7,450	280	215	1,260	79,350	41	80	64	76
f	6,330	242	215	1,150	67,000	41	71	65	63
g	3,300	185	750	880	49,800	38	170	61	41
Hole 332B									
a	2,260	120	318	660	41,220	37	91	71	35
b+	6,825	246	61.5	1,370	80,960	38	58	70	82
c									
d	6,290	224	215	1,160	67,710	50	74	66	68
e				scattered					
f	5,080	167	360	1,186	75,170	44	147	81	68
g	6,917	243	185	1,282	75,340		82	60	76
h				scattered					
i	3,320	160	335	1,000	57,000	37	125	71	45
j				scattered					
k				scattered					
Site 334									
a	5,160	250	265	1,220	71,200	43	116	72	74
b	4,440	240	190	1,240	70,000	47	84	88	70
Site 335									
	6,900	260	340	1,280	73,900	43	152	60	72

$$\frac{F_1}{F_2} = (\frac{E_1}{E_2}) \, \overline{PE\text{-}1} \quad \text{for an element } E$$

if we choose E as an element with low partition coefficients (e.g., Ti), $1/(PE\text{-}1)$ will have little variation in the model: this way, the model assumed above has little importance in the value of F_1/F_2; it is possible to determine P_{Ni} using:

$$P_{Ni} = \frac{\log \dfrac{Ni1}{Ni2}}{\log \dfrac{F1}{F2}} + 1$$

With chemical unit c and b, we find $Fc/Fb = 1.25$ *and* $PNi = 2.27$ with chemical units c and e1, we find $Fc/Fe1 = 1.34$ and $P_{Ni} = 2.22$ taking into account the slope found $P_{Cr-1}/P_{Ni-1} = 2.35$, we find $P_{Ni} = 3.91$.

These values of 2.25 for P_{Ni} and 3.91 for P_{Cr} are in agreement with the values calculated from the mineral partition coefficients and the simple model proposed above (2.37 and 4.04, respectively).

To calculate the quantity of liquid remaining after crystallization even if Ni and Cr initial liquid concentrations are thought to be independent of partial melting process, it is necessary to assume initial values in the liquid for these elements. From the model mentioned for partial melting (Allègre et al., 1973) these values

should be 250 ppm for Ni and 600 ppm for Cr, which correspond to the richest glasses of the FAMOUS area which plot on the right of the line of Figure 7. Early removal of olivine (1%-2%) from this liquid gives the composition of the richest Ni-Cr samples lying on the straight line, 165 ppm for Ni and 600 ppm for Cr; we will assume these values for the initial liquid (just after early removal of olivine) the slope of the straight line log Cr versus log Ni being representative as mentioned above of an average crystallization of 60% plagioclase, 25% augite, 10% orthopyroxene, and 5% olivine. Thus, the percentage of remaining liquid is obtained using:

$$F = (\frac{Ni}{165}) \, \frac{1}{1.24} \quad \text{or} \quad F = (\frac{Cr}{600}) \, \frac{1}{3}$$

The values obtained using the first or the second expression (Ni or Cr) are indicated in Table 2 and the average value of both values. Crystallization $(1\text{-}F)$ varies between a few percent to 50%-55%; highly phyric plagioclase basalts from the top of Holes 332A and 332B (a units and i unit of 332B) are little differentiated; plagioclase phyric units f of Hole 332A and d of Hole 332B would be representative of some 30% of crystallization as well as the plagioclase phyric sample of unit k of Hole 332B.

Aphyric samples are the most differentiated (40%-50%). Olivine phyric samples would plot on the right of the straight line (high olivine content) with chromium

TABLE 2
Ni, Cr, Ti Values of Aphyric Units, or Calculated in the Groundmass
(for Plagioclase Phyric Units)

Chemical Unit	Plag. Content	Ni	Ni Corr.[a]	F_{Ni} $(\frac{Ni}{165})^{1.24}$	Cr	Cr Corr.	F_{Cr} $(\frac{Cr}{600})^{\frac{1}{3}}$	F	Ti	Ti Corr.	Ti_0 $Ti\times(F)^{-.92}$
Hole 332A											
a	0.3	83	118	0.76	292	416	0.88	0.82	2340	3342	2784
b		55		0.41	64		0.47	0.44	6920		3251
c		73		0.52	113		0.57	0.55	5460		3150
d		65		0.47	82		0.51	0.49	6480		3361
e1		51		0.39	54		0.45	0.42	7390		3326
e2	0.03	81	83.5	0.58	215	222	0.72	0.65	7255	7480	5032
f	0.15	71	84	0.58	215	252	0.74	0.66	6290	7391	5042
Hole 332B											
a	0.3	91	130	0.82	318	454	0.91	0.87	2260	3230	2841
b c		51		0.39	61		0.47	0.43	6885		3167
d	0.13	72.5	83	0.57	230	264	0.76	0.67	6300	7240	5008
f		147		0.91	360		0.84	0.88	5080		4516
g		82		0.57	185		0.67	0.62	6917		4455
i	0.20	125	156	0.95	444	550	0.97	0.96	3320	4150	3997
k	0.15	71	84	0.58	212	250	0.74	0.66	5440	6400	4366
Site 334											
a		116		0.75	265		0.76	0.76	5160		4008
b		84		0.58	190		0.68	0.63	4440		2902
Site 335											
		152		0.93	340		0.83	0.88	6900		6131

Note: F_{Ni} and F_{Cr} are the calculated remaining liquid fractions after crystallization using Ni or Cr values; F is the average value of F_{Ni} and F_{Cr}. Ti_0 is the calculated Ti concentration in the initial liquid.

[a]Corr. means corrected for plagioclase content.

values around 600 ppm: since Cr olivine partition coefficient is close to 1, if olivine crystals are in equilibrium with the groundmass, it could be concluded that these samples are little differentiated in respect of the primary liquid.

Partial Melting

It is clear that if all samples are descended from initial liquids produced by identical partial melting, from high values to small values of Cr and Ni, Ti should increase in a continuous way. As indicated in Figure 4, this is not correct and if Ti has the same behavior as LPC elements, as previously mentioned, this means that Leg 37 samples come from initial liquids descended from different degrees of partial melting. Ti concentrations in initial liquids can be calculated from Ti concentrations of samples and the percentage of remaining liquid which they represent calculated from Cr and Ni data. These calculated initial values are indicated in Table 2; we have no more than two or three groups of values, one around 3000 ppm and the other around 4000 to 5000 ppm: this is consistent with the assumption that the number of magmas is necessarily limited below a given area of the rift valley. The value of 2800 ppm found for highly phyric plagioclase units (a of Holes 332A and 332B) indicates a high partial melting probably higher than 20% (maybe up to 25%), and the

values of 5000 ppm indicate a partial melting around 18%, the figures given depending on the model used for partial melting.

Results obtained for transition elements are in agreement with other studies of trace elements: for example, unit a of Holes 332A and 332B have low values of Zr-Y (Lambert and Holland, this volume) which agree with the small degree of crystallization found, and aphyric units b, c, d, and e1 of Hole 332A have the highest values of Zr-Y corresponding to highest degree of crystallization found.

For partial melting, samples from Holes 332A and 332B (Lambert and Holland, this volume) seem to plot in a Zr-Y diagram on two straight lines passing through the origin, with different slopes, indicating two different magmas originated from different partial melting—this agrees with the two groups of Ti initial values found. However, a discrepancy remains between both studies: from Ti initial values, aphyric units (b, c, d, e1 of Hole 332A and b, c of Hole 332B) are in the group of 3000 ppm, similar to unit a of Holes 332A and 332B, and all these samples do not plot on the same straight line in the Zr-Y diagram; rare earth data (Puehelt et al., Schilling et al., Bryan et al., this volume) seem to be in agreement with the Zr-Y data.

At Site 334 the values of Ti in initial liquids from which are derived units a and b are 3960 and 2900 ppm,
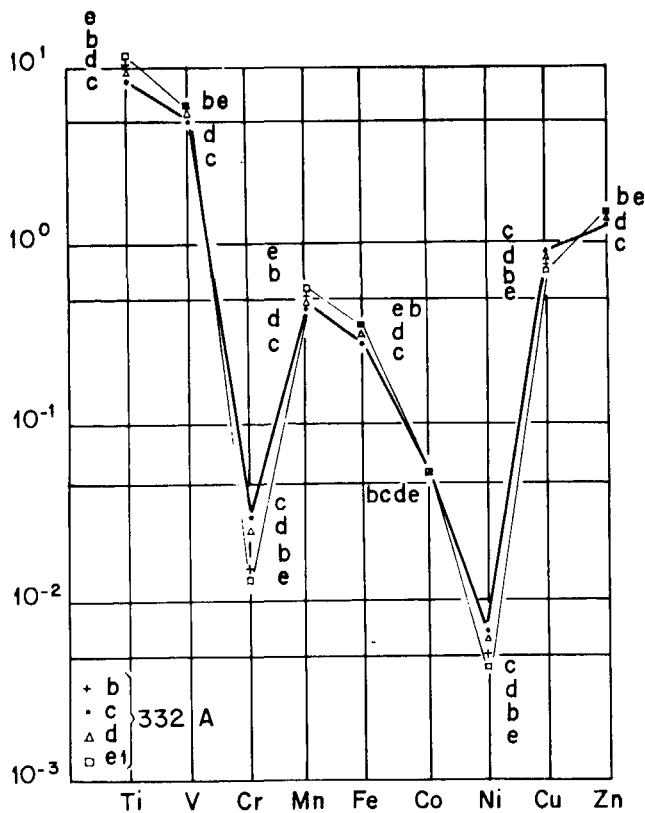
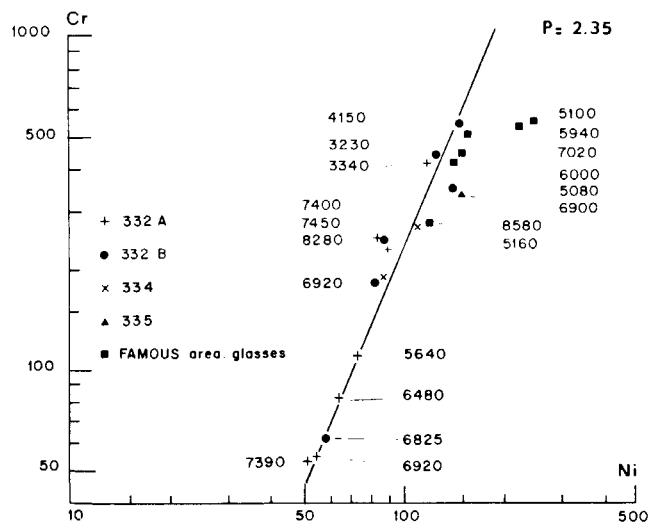Figure 6. *Hole 332A; b, c, d, el chemical units: Chondrite-normalized diagram.*

Figure 7. *Log Cr versus log Ni. Glasses, aphyric samples or plagioclase phyric samples corrected for their plagioclase content. Figures mentioned correspond to Ti concentrations.*

respectively. In this case, the b unit plots in the same field in the Y-Zr diagram as other samples of the 3000 ppm Ti initial values (Lambert and Holland, this volume), indicating a high degree of partial melting. In the unit c, the concentrations found for gabbros permit them to be considered as the solid phase expression of crystallization. Ti and V on one hand (LPC elements)

and Cr and Ni on the other (HPC elements) vary in the opposite direction. Peridotites of Site 334, thinking only in terms of geochemical behavior of trace elements, can be considered either as a residual phase of partial melting, or as crystallization products from a magma; if they are a crystallization product, as suggested by their cumulate feature, they must derive from a magma produced by a high degree of partial melting to be in agreement both with low Ti-V values and low rare earth values (Dostal and Mueke, this volume).

CONCLUSIONS

The following points are enhanced from the first transition series elements:

1) The concentrations found in aphyric samples or in the groundmass are in agreement with partition coefficients.

2) Samples can be classified in the same way as they were onboard from major elements.

3) Different degrees of fractional crystallization (from a few percent up to 55%) are shown from Cr and Ni data.

4) Ti values calculated for the initial liquids show different steps of partial melting (15%-25%).

REFERENCES

Allègre, C.J., Javoy, M., and Michard, G., 1968. Etude de l'abondance des Eléments de transition dans l'écorce terrestre, comparée à celle des terres rares. In Ahrens, L.H. (Ed.) Origine et distribution des éléments: New York (Pergamon Press), p. 914-928.
Allègre, C.J., Montigny, R., and Bottinga, Y., 1973. Cortège ophiolithique et cortège océanique, géochimie comparée et mode de genèse: Soc. Géol. Fr. Bull., v. 7, p. 461-477.
Bougault, H. and Hékinian, R., 1974. Rift valley in the Atlantic ocean near 36°50'N: Petrology and geochemistry of basaltic rocks: Earth Planet. Sci. Lett., v. 24, p. 249-261.
Burns, R.G., 1970. Site preferences of transition metal ions in silicate crystal structures. In Geochemical application of crystal-field theory: Chem. Geol., v. 5, p. 275-283.
Curtis, C.D., 1964. Application of the crystal field theory: the inclusion of trace transition elements in minerals during magmatic differentiation: Geochem. Cosmochim. Acta, v. 28, p. 389-403.
Montigny, R., Bougault, H., Bottinga, Y., and Allègre, C.J., 1973. Trace element geochemistry and genesis of Pindus ophiolite suite: Geochim. Cosmochim. Acta, v. 37, p. 2135-2148.
Orgel, L.E., 1964. Chimie des éléments de transition. Dunod Ed., Paris.
Ringwood, A.E., 1966. Mineralogy of the mantle. In Harley, P.M. (Ed.), Advances in earth sciences: Boston (M.I.T. Press), p. 357-399.
Shaw, D.M., 1970. Trace element fractionation during anatexis: Geochim. Cosmochim. Acta, v. 34, p. 237-243.
Treuil, M., 1973. Critères pétrologiques, géochimiques et structuraux de la genèse et de la différentiation des magmas basaltiques: exemple de l'Afar: Thèse, Université d'Orléans.